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"NEW METHODS FOR SOLID STATE EXTRUSION OF HIGHLY ORIENTED POLYMERS"

by

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INTRODUCTION

The development of thermoplastics of high tensile modulus has been the subject of intense research in recent years. This can be achieved by introducing a high degree of chain orientation and extension by solid state deformation of semicrystalline polymers by the processes of drawing (1) and extrusion (2).

Work in this laboratory originated in studies of the crystallization of an oriented high density polyethylene (HDPE) melt using an Instron capillary rheometer (3). It was found that these polyethylene rods had a remarkably high modulus (up to 70 GPa) (4). The process was modified to a solid state extrusion by Capiati, et al. (5), in that melt crystallized billets of HDPE were extruded below their melting point through conical dies of draw ratio up to 40. Mead (6), Kojima (7) and Perkins (8) studied the effect of varying processing conditions on properties and observed the range of materials that may be prepared by this method.

We wish to review here a series of developments made in this laboratory that have extended the range of the solid state extrusion technique for HDPE and also allows the extrusion of materials previously found to be difficult to process by conventional solid state extrusion. The properties of materials produced by these unconventional processing methods will also be described. The topics to be discussed are:

Section 1. Extrusion of High Density Polyethylene

(a) Conventional Solid State Extrusion
(b) Split Billet Extrusion
(c) Push-Pull Extrusion

Section 2. Processing of "Unprocessable" Polymers

(a) Conventional Solid State Extrusion
(b) Powder Extrusion
(c) Solid State Coextrusion

Section 3. Properties of Oriented Ultrahigh Molecular Weight Polyethylene Prepared using the Powder and Coextrusion Techniques

Section 4. The Use of Ammonia as a Plasticizer for Nylon 6 in Solid State Extrusion

Summary

Section 1. Extrusion of High Density Polyethylene

(a) Conventional Solid State Extrusion

The processing and properties of HDPE rods produced by solid state extrusion will be briefly described; for more detail, the reader is referred to the original papers (6-8) and an extensive review by Zachariades, et al. (9). The polyethylene used was a duPont grade Alathon 7050 $\bar{M}w$ = 57,000, $\bar{M}w/\bar{M}n$ = 3. Melt crystallized billets were prepared by melting at 160°C and subsequent crystallization under the combined effects of temperature and pressure. The billets were extruded through a conical brass die, with an included entrance angle of 20°, in a 3/8" bore Instron capillary rheometer.

Figure 1 shows that as the draw ratio increases the apparent viscosity increases and hence the extrusion rate drops rapidly. The rapid increase in viscosity is thought to be related to the strain hardening observed in a conventional tensile test at high elongation (10). The extrusion rate is promoted by high extrusion pressure, however, there is an upper limit to the pressure. When the pressure is increased much above 0.23 GPa, stick-slip extrusion occurs. At an extrusion pressure of 0.23 GPa, the extrusion stops when the viscosity increases sufficiently that the extrusion force cannot overcome the resistance to extrusion. During slip in stick-slip extrusion, a spiral fractured extrudate is produced that is similar to spiral products found in shear fracture of polymeric melts during extrusion (12). The flow profile in the solid state extruded rods is a deep shear parabola (10, 13, 24) (Figure 2) which suggests that stick-slip may arise from

shear fracture of the extrudate.

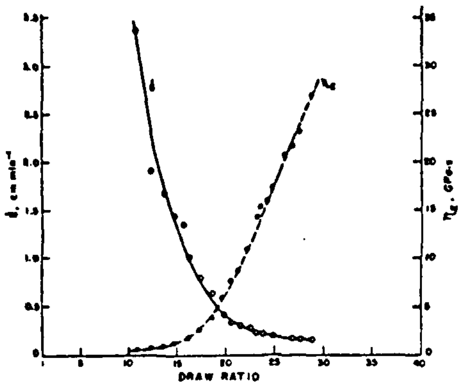


Figure 1: The relaxation between viscosity, extrusion rate and draw ratio for low molecular weight HDPE (Alathon 7050).

Figure 2: Shear flow profile for low molecular weight HDPE (Alathon 7050) at extrusion draw ratio 24.

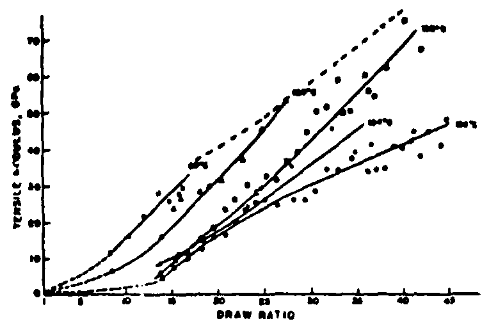


Figure 3: Variation of modulus with extrusion draw ratio at a series of different extrusion temperatures, extrusion pressure 0.23 GPa. The dashed line indicates the maximum draw ratio attainable. Ref. 14.

The range of moduli and draw ratios available by this process is shown in Figure 3. The moduli are measured at 0.1% strain and a strain rate of 2.0 x 10^{-5} sec^{-1}. The lower the extrusion temperature, the higher the modulus, presumably because of greater efficiency of deformation. Efficiency of deformation is the ratio of the bulk deformation to the deformation of the individual polymer chains. However the maximum available draw ratio is also dependent on temperature such that the maximum modulus is observed for samples extruded at 132°C and a draw ratio of 40. The physical properties of the extruded rods are given in Table 1, and a comparison with other high modulus materials is made in Table 2.

TABLE 1

Comparison of Physical Properties of Ultraoriented HDPE Rods with Single Crystal Material

Physical Property	Polyethylene Single Crystal	Ultraoriented PE Rod
Tensile modulus GPa	285, 240 (47,48)	70
Strain to fracture %	6 (49)	3%
Tensile strength GPA	13	0.4
Linear Expansion Coefficient, 10^{-5} $^{\circ}C^{-1}$	(a)-axis + 22 (50) (b)-axis + 3.8 (c)-axis -1.2	-0.9 ± 0.1 Fiber axis
Melting point, $^{\circ}$C	145.5 (51)	139°C (10°C min^{-1} heating rate)
Crystallinities		85%
Crystal orientation function	1.0	0.996 ± 0.502
Birefringence total	0.059 (52)	0.0637 ± 0.5015

TABLE 2

Presently Achievable Polymer Tensile Properties

Material	Tensile Modulus (GPa) Small Crystals	Tensile Modulus (GPa) Bulk Samples	Tensile Strength (GPa)
Polypropylene	42 (48)	22 (53)	0.93 (53)
Polyethylene	240 (48)	70 (54,55,56)	0.60 (58)
Polystyrene	12 (48)	4.5 (57)	0.08 (57)
Carbon Steel SAE 1020	208 (59)		0.45-0.62 (59)
Aluminum	69 (59)		0.09-0.17 (59)
Glass Fiber	69-183 (60)		0.39-0.69 (59)

Detailed analyses of the properties of highly oriented HDPE have been made by Mead and Porter (14), Farrell and Keller (15), Ward and coworkers (16). A model for the morphological changes in highly drawn and extruded polyethylene has been proposed by Peterlin (17), alternate models have been proposed by Clark and Scott (18) and Porter (19). The key to the high modulus of these morphologies seems to be in the high modulus of the PE unit cell (~ 230 GPa) (20,48). The PE chain crystallizes in the trans-trans conformation so that only bending and extension of carbon-

carbon bonds can occur, and the crystallized chain has a very high modulus in the chain direction. Clearly the solid state extrusion technique is very efficient in producing high modulus HDPE, and hence the interest in extending the range of the extrusion technique.

(b) Split Billet Extrusion

The first departure from conventional extrusion came with the invention of the split billet technique (21). A melt crystallized billet of HDPE (Alathon 7050) was split in half longitudinally (Figure 4); the two halves are then placed together and extruded through a conventional conical brass die. The flow profiles in Figure 2 were obtained by marking the inside surface of the split billet. Figure 5 shows the effect of splitting the billet on the extrusion rate. Initially the conical part of the billet is extruded so the draw ratio of the extrudate steadily increases until the cylindrical part of the billet is reached and "steady state" extrusion occurs with the extrudate having a constant draw ratio. Clearly the split billet extrusion proceeds at a higher rate and, perhaps more importantly, the maximum draw ratio obtainable without fracture was increased. This is thought to be due to stress relief from the addition of a free surface in the center of the billet (21). The products from the split billet extrusion are indistinguishable from conventionally extruded Alathon 7050 rods processed under the same conditions. The increased draw ratio available using this technique is illustrated in Figure 6, a plot of extrusion draw ratio against extrusion temperature.

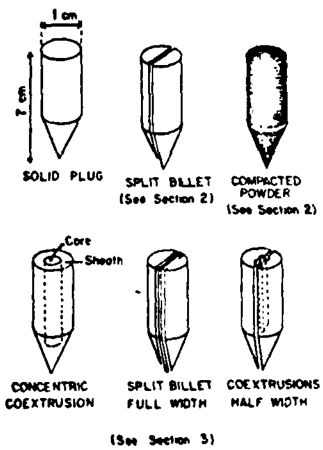


Figure 4: Schematic of the different sample geometries used in this study.

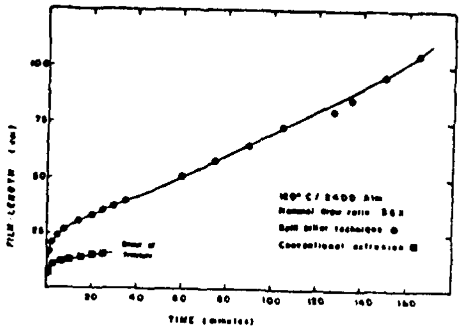


Figure 5: A comparison of the extrusion rate for a split billet and solid plug extrusion. Ref. 21.

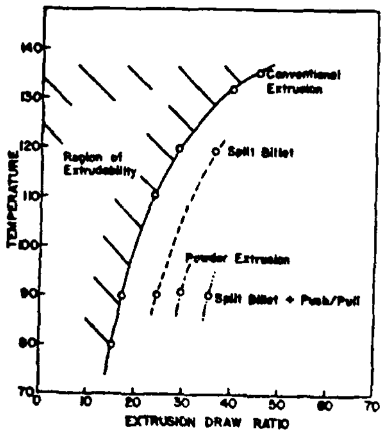


Figure 6: Processing map for Alathon 7050, extrusion pressure 0.23 GPa. Lines connect points of maximum draw ratio available at given draw ratio.

At a given temperature, there is a maximum draw ratio that can be successfully extruded. The lines in Figure 6 join up these points of maximum draw ratio. Above 138°C the extrudate melts at the die exit, hence, a region of extrudability can be drawn. The dashed line shows the limit of extrudability for the split billet technique, i.e. the split billet allows new regions of the temperature/draw ratio map to be studied.

(c) Push-Pull Extrusion

Pulltrusion processing is common in metals and polymer composites. The extrusion process used in this laboratory has a possibility of extruding the polymer under a combined push force and pull load by attaching weights to the emerging extrudate. The effect of pull load on the extrusion of Alathon 7050 split billets has been studied (11). Figure 7 shows the marked increase in extrusion rate produced by adding a pull load to the extrudate. The effects of push force and pull force on extrusion rate are superimposable.

Push force = 3X (Pull Force)

The factor 3 arises from the hydrostatic transmission of forces through the polymer in the die. When too large a pull force is used, the extrudate fractures at the base of the conical part of the die (Figure 7). From the relationship between push and pull forces, the pressure at the base of the conical part of the die may be calculated (0.08 GPa). This is similar to the tensile strength of the extrudate (0.04 GPa) at the extrusion temperature. Although the extrusion proceeds under compression, the material is being elongated in the die, hence the correspondence between the pressure at fracture and tensile strength.

In conventional extrusion the maximum pressure that can be applied without stick-slip is around 0.23 GPa and so this provides

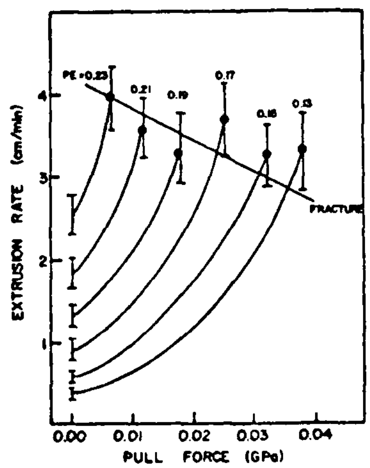


Figure 7: The effect of the addition of a pull force on extrusion rate at a series of different extrusion pressures (PE). Addition of the pull load increases the extrusion rate until fracture occurs in the die; marked • on the graph. The polymer is a split billet of Alathon 7050, extrusion draw ratio 36. temperature 120°C.

a "process dependent" restriction on extrusion rate and the maximum draw ratio available. In push-pull extrusion, forces up to the tensile fracture of the material can be applied so the true maximum draw ratio for the material at a given temperature can be obtained. The limit of temperature and draw ratio detected in these studies has been added to the extrudability map (Figure 6) showing the maximum regions of the temperature/draw ratio map that may be studied. Clearly the push-pull process greatly extends the range of the extrusion technique. A series of samples prepared at the same draw ratio and temperature, but with different combinations of push and pull, have the same modulus, i.e. mechanical properties are independent of the applied pressure.

Section 2. Processing of "Unprocessable" Polymers

This section deals with semicrystalline thermoplastics that cannot be processed by the techniques described earlier. Perkins and Porter (22) have reviewed the solid state deformation of polymers in detail and describe the numerous reports of solid state extrusion. Aharoni (23) has reported that a number of polymers may be solid state extruded to high draw ratio (> 10) by the conventional process. These include HDPE, poly(ethylene oxide), poly(4-methyl pentene 1). Poly(propylene) is also readily extrudable (24). However, there are many other polymers that would be attractive if they could be obtained in high draw, particularly the established fiber-forming polymers such as the nylons and poly(ethylene terephthalate). The maximum extrusion draw ratio that has been reported for nylon 6 is 5 (25). This has been attributed to the onset of strain hardening at much lower extensions than polyethylene (10). Ultrahigh molecular weight polyethylene is also of interest as a way of improving the mechanical properties of the polyethylene rods.

We will describe some new developments which allow these materials to be extruded to higher draw ratios. Details of the polymers described in this section are given below.

TABLE 3

Polymers Used in This Study

Polymer	Producer	Grade	$\overline{M}_w$
High density Polyethylene	DuPont	Alathon 7050	59.000
Ultrahigh molecular weight Polyethylene	Hercules	UHMW 1900	5×10^6
Nylon 11	Rilsan	Besno	28×10^3
Poly(ethylene terephthalate)	Goodyear	VFR 5041 VFR 5610	IV = 1.04 IV = 0.6
Poly(styrene)	Monsanto	HH 101	333×10^3
Poly(vinylidene fluoride)	Kureha, Japan	—	—

(a) Conventional Solid State Extrusion

We have attempted to extrude nylon 11, poly(ethylene terephthalate) (PET) and ultrahigh molecular weight polyethylene (UHMWPE). The billets were prepared by slow cooling from the melt. The results are summarized below. Nylon 11 was extruded up to draw ratio 5 in the presence of silicone oil lubricant. Both high molecular weight PET and UHMWPE could not be extruded at this draw ratio. Use of the split billet and push-pull techniques did not assist the extrusion. For the purposes of this discussion these polymers will be described as "unprocessable".

TABLE 4

Conditions for Conventional Solid State Extrusion of Some Fiber Forming Polymers at Draw Ratio 5

Polymer	$T_m/^\circ C$	$T_{ext}/^\circ C$	P_{ext}/GPa	Ext. Rate cm min^{-1}
UHMWPE	134	120	0.23	S-S
Nylon 11 no lubricant	194	180	0.23	S-S
Nylon 11 silicon oil lubricant		120	0.16	2.0*
PET IV = 1.04	270	260	0.4	S-S
IV = 0.6	270	250	0.23	1.0*

S-S indicates that stick-slip occurred

(b) Powder Extrusion

First we discuss the extrusion of a compacted powder. Powder processing is used extensively for metals and ceramics. There are only a few investigations and applications to polymers. PTFE (26) is processed as a granular powder in molding and extrusion processes. The compacted powder is heated to the gel state, shaped, and allowed to solidify in the mold. A patent claiming the use of powdered UHMWPE for processing above the melting point (28) and a paper describing the compaction of these powders have also appeared (29).

This development involves the extrusion of a compacted powder billet prepared and extruded below the melting point. The powder is loaded into the 3/8" diameter barrel of an Instron capillary rheometer that is plugged at one end. A moderate pressure (~ 0.23 GPa) is applied to compact the powder into a coherent billet. This billet is then extruded in the conventional manner giving a translucent coherent strand.

A sample of powdered Alathon 7050 was prepared by precipitating a solution in xylene into methanol. The compacted billet was extruded at draw ratio 30 and at 90°C, conditions that are unattainable in conventional extrusion (6) (Table 5). This data can be added to the extrudability map (Figure 6) and shows that using a powder is not as efficient at promoting the extrusion as the push-pull process. There is also some loss of properties in the powder extrudate (Section 3).

UHMWPE is available commercially as a powder and if it is prepared as a compacted billet as above, it may be extruded up to DR 24 at 128°C whereas a solid plug or split billet cannot even be extruded to DR 5, a major change in extrudability (30). The properties of these products are described in Section 3.

Conventional extrusion is thought to proceed by extension of an entangled molecular network. There is no molecular network between powder particles so the particles are thought to be deformed by interparticle adhesion and friction. Moreover, it is this lack of molecular entanglement that improves the extrudability.

As well as offering a way of handling difficult materials, this technique provides access to entirely new morphologies (29). A large quantity of solution grown single crystal mats of Alathon 7050 was prepared from xylene solution. These were packed into the rheometer and extruded. The presence of the highly structured single crystal gave a further improvement in the extrusion rate. Details of the processing and properties are the subject of a separate publication (29).

TABLE 5

Conditions for Extrusion of UHMWPE by the Powder and Coextrusion Processes

Sample	Ext. Draw Ratio	Pres./GPa	Tem./°C	Pres./GPa	Tem./°C	Rate cm min^{-1}
Alathon 7050 Powder Extrusion	30	0.23	90	0.23	90	0.06
UHMWPE Powder Extrusion	24	0.23	128	0.23	128	0.2
UHMWPE* Coextrusion High Pressure Cryst.	5	0.15	180	0.15	120	2
UHMWPE* Coextrusion Low Pressure Cryst.	5	0.46	210	0.20	120	2

*Nylon 11 sheath was prepared by melting at 230°C and crystallized by cooling slowly under 0.1 GPa pressure.

(c) Solid State Coextrusion

The coextrusion processes are the second group of methods for processing "unprocessable" polymers. They subdivided into split billet coextrusion and concentric billet coextrusion. In principle they involve the extrusion of the unprocessable component in a sandwich with a processable polymer, to promote extrusion. A form of substrate drawing.

Split Billet Coextrusion. During the development of the split billet technique, it was realized that by placing a polymer film between the billet halves, the film would be extruded with the outside halves and ultradrawn thin film could be produced (Figure 4). 0.1 mm thick films of Alathon 7050 draw ratio 24 were produced at 120°C, a draw ratio that was unobtainable using a slit die. The film in the center of the billet is forced to follow the two outside halves because of the compression in the conical die and friction between the components.

This technique was then applied with poly(vinylidene fluoride) films to a maximum draw ratio of 7 at 120°C. PVF_2 was of interest because of its piezoelectric properties, the films had a moderate modulus, and complex melting behavior (31,32).

Alternatively a film of amorphous polystyrene was placed in a HDPE split billet and when extruded at 126° to draw ratio 12 gave a thin oriented film. This film had a fibrous structure and is the first report of an amorphous polymer having a microfibril morphology (33).

These examples show how versatile the split billet coextrusion process is in producing oriented thin films.

Further insight into the coextrusion process has developed from work on amorphous polyethylene terephthalate films. Films of amorphous PET were prepared by melt pressing at 280°C and quenching in ice water. These were then extruded at 100°C in an Alathon 7050 split billet. Unoriented amorphous PET does not crystallize at a significant rate at this temperature (34). On extrusion through a draw ratio 7 die, films 0.5 mm and 1.0 mm thick emerged with draw ratio 7. However, a film 2.0 mm thick emerged with a draw ratio of 5, insufficient compressive forces were transmitted by the two polyethylene halves to the thick film. For the film and substrate to undergo the same strain, the total stress in the film and substrate must be similar and the total stress in film may be controlled by the cross sectional area.

Attempts to extrude 1.0 mm thick films of amorphous PET at draw ratio > 7 failed because of fracture at the edges of the film. All the film extrusions discussed so far involve films that are the same size as the flat surface of the split billet. A 1.0 mm thick film of PET was cut so that it was 1/2 the width of the billet surface and positioned in a groove in the center of the billet (Figure 4). Using this configuration, a coherent film of draw ratio 12 was obtained, nearly double the previous value.

This illustrates the second important feature of coextrusions. The flow profile of a full width Alathon 7050 film is a deep shear profile, the same as the split billet (21) (Figure 2), i.e. the edges of the film undergo severe shear stress. In contrast, a film that covers only the central part of the billet will undergo essentially extensional deformation. The shear strength is lower than the tensile strength, particularly in highly drawn materials, so the full size PET film undergoes fracture at the edges whereas the half size films do not and may be taken to much higher draw.

These examples illustrate the use of the split billet coextrusion process for film extrusion and show some of the factors that are important in optimizing the process.

Concentric Billet Coextrusion. The concentric billet extrusion uses a billet of processable polymer with a hole drilled in the center. A rod of "unprocessable" polymer is placed in this hole and the composite extruded (Figure 4). The concentric composite billet was first used to prepare "one polymer composites" in which the two components consist of two samples of HDPE of different molecular weight (35). Many features of these composites have been studied (36,37).

In the case of a concentric billet consisting of two different polymers, the outer sheath can act merely as a processing aid

and/or polymer die. After extrusion it is removed to leave the core component.

The concept is illustrated by the processing of ultrahigh molecular weight polyethylene. The outer sheath was a melt crystallized billet of nylon 11 that could be extruded to draw ratio 5 at 120°C and 0.16 GPa using a silicone oil lubricant. Two samples of UHMWPE were prepared. The UHMWPE was melt crystallized in the rheometer at two different temperatures and pressures. The low temperature, low pressure conditions were chosen so as to prepare a lamella morphology; the high temperature, high pressure conditions to give a chain extended product (38) (Table 5). The billets were machined so that they fitted inside the nylon 11 sheath. The composite was extruded at draw ratio 5 and 120°C. The nylon casing was removed to free the core which was a coherent fracture free rod. The presence of the outer sheath allowed UHMWPE to be extruded to a higher draw than is possible by conventional extrusion.

The nylon casing is extruded with the core; therefore there is no shear at the surface of the core. Also, the material at the center of the billet does not undergo shear deformation as much as the surface in contact with the rheometer walls, so again shear stresses are minimized and shear fracture (stick/slip) prevented. These features are the same as for split billet coextrusion. In addition, the sheath has significant tensile strength perpendicular to the chain direction, hence the core is held under a significant compressive force after the sample has left the die. This insures plastic rather than elastic deformation of the core. The importance of the tensile strength of the sheath is illustrated by an attempt to extrude an UHMWPE core and a low molecular weight HDPE sheath - the sheath fractured.

The possibility of using other casings so as to increase the draw ratio is under investigation, as is the possibility of using a molten core in a solid casing.

Section 3. Properties of Oriented Ultrahigh Molecular Weight Polyethylene Prepared Using the Powder and Coextrusion Techniques

The mechanical properties of oriented UHMWPE are used to indicate that polymers that require unconventional processing may also have unconventional properties. Details are given elsewhere (30).

Expiremental

The mechanical properties of extruded rods were measured in tension in an Instron TTM tester at a strain rate of 2×10^{-5} sec^{-1}. The tangent modulus at 0.1% strain is recorded. The degree

of crystallinity was measured on a Perkin Elmer DSC 1B at a heating rate of 10°C min^{-1} using Indium calibration and a heat of fusion of 69 cal g^{-1}.

Powder Extruded UHMWPE

The principal properties of an UHMWPE powder extrudate with draw ratio 24 are given in Table 6. The most obvious feature of the rods is that they are opaque whereas rods of Alathon 7050 from melt crystallized billets are transparent. The density of the powder extruded rod was 0.96 gcm^{-3}, a value consistent with the degree of crystallinity of 70%. This indicates that the opacity is a result of minute density fluctuations rather than the presence of gross voids. The tensile modulus is lower (15 GPa) than the modulus of Alathon 7050 melt crystallized, and drawn to a draw ratio of 24 (25 GPa). However, this is a substantial increase over unoriented material. Clearly significant orientation and chain extension has occurred during extrusion. Tensile strength was lower than Alathon 7050 but elongation at break was the same.

TABLE 6

Mechanical Properties of UHMWPE Products

Sample	Draw Ratio	Tensile Modulus/ GPa	Tensile Strength/ GPa	Elongation at Break %	Degree of cryst. %
Alathon 7050 Solid billet	24	25	0.25	3	85
UHMWPE Powder extrusion	24	15	.11	2	76
Alathon 7050 Solid billet	5	6.9	.3	3	80
UHMWPE Coextruded low pressure cryst.	5	.712	.07	32	60
UHMWPE Coextruded high pressure cryst.	5	6.7	.2	13	78

Coextruded Products

The extrudate prepared from the billet crystallized at high temperature and pressure had tensile modulus and strength comparable with Alathon 7050 if the same draw, but the elongation at break (12%) was much larger than Alathon 7050 (3%).

The extrudate from the billet crystallized at low temperatures and pressures was completely different. This sample was transparent and had the "feel" of a rubber. Figure 8 shows that a sharply bent sample of the "rubbery" material maintains its clarity, whereas an extrudate of Alathon 7050 shows stress crazing. The bend is recoverable in the rubbery material but not in Alathon 7050.

The mechanical data for this rubbery material are a low modulus (0.71 GPa), low tensile strength (0.07 GPa) and high elongation to break (30%). A yield point was not found and the majority of the elongation was reversible (20%). These are most unusual properties for polyethylene.

The high elongation to break of the UHMWPE extrudates from melt crystallized billets is a result of the high molecular weight of the polymer. The low elongation at break of the powder extruded product is presumably due to regions of weakness between the compacted and elongated powder particles. The big differences between the coextruded products prepared under different crystallization conditions is presumably due to morphological differences. These are under investigation.

Section 4. The Use of Ammonia as a Plasticizer for Nylon 6 in Solid State Extrusion

The nylon family has a wide industrial application and plasticizers have been used in their processing (39,40). Even so, the prominence of hydrogen bonding between amide groups of adjacent chains makes their processing feasible only at relatively low molecular weight and high temperatures. Consequently, the choice of plasticizer depends, among other variables, on ability to withstand high processing temperature and to interrupt the interchain hydrogen bonding. Compounds effective in nylons are thus generally polar and of low volatility. A disadvantage of using such additives is that the plasticizer remains in the nylon thus tending to depress the mechanical properties. Therefore, it would be generally desirable to remove the plasticizer after processing. Volatile plasticizers can aid in processing yet be subsequently removed for enhanced final properties, however they are not readily handled in conventional drawing process.

Anhydrous ammonia has been previously used for the plasticization of wood (41,42). It further appeared to be a suitable plasticizer for the solid state extrusion of nylons. This is because it may be readily retained in the sample under pressure during

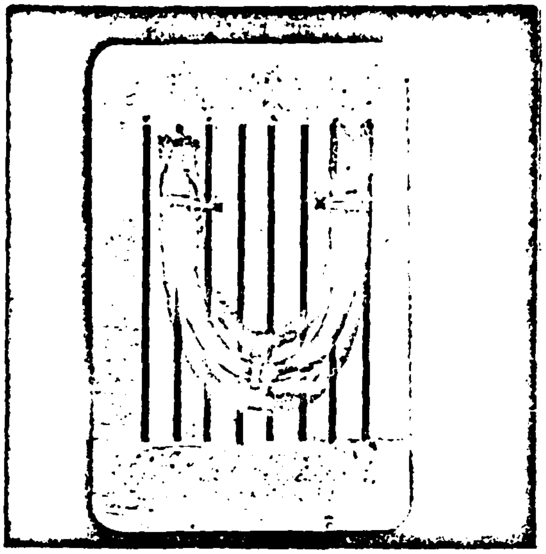
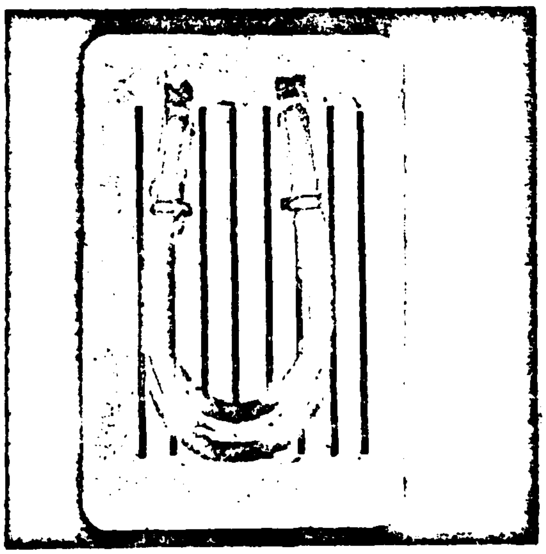


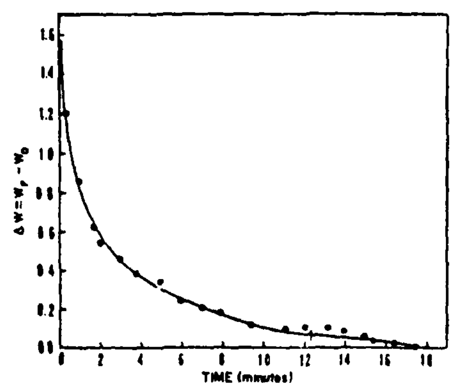
Figure 8: The flexibility of the "rubbery" UHMWPE prepared by by low pressure crystallization and coextruded (top) is compared to that of conventionally extruded Alathon 7050 (bottom).



extrusion and removed after the deformation process has occurred. Under the conditions of our studies its incorporation in preformed nylon fibers prior to extrusion alleviates significantly the processing difficulties encountered with untreated nylons and provides rapid extrusion of highly oriented extrudates. According to our technique, nylon ribbons (M_w = 16,000) 0.18 mm thick and 9.5 mm wide were exposed to ammonia at room temperature for 5-6 hours in a pressure vessel in which the relative vapor pressure of ammonia was 1 MPa. Thermogravimetric analysis showed that the amount of ammonia absorbed by the nylon 6 was ~18 wt % (see Figure 9) and that the rate of desorption, after pressure removal, increased with temperature.

The originally translucent films were treated with ammonia and inserted within longitudinally-split high density polyethylene billets (M_w = 59,900) which were previously chilled in liquid nitrogen. The assembly was loaded in an Instron rheometer and extruded through a conical brass die of included entrance angle of 20° and nominal extrusion draw ratio (EDR) 12. The extrusion pressure was 0.20 GPa and the temperature 95°C i.e. 124°C below the melting point of nylon 6. On exiting the extrusion die, the ammonia volatilized quantitatively from the deformed nylon 6. For comparison, experiments were conducted with untreated nylon 6 films under the same extrusion conditions, but the attempts were unsuccessful in that no nylon extrusion occurred at the same or higher pressures.

Figure 9: Desorption of ammonia as a function of time at 50°C, expressed by the weight loss (mg) of the nylon sample. W_F is the weight of sample during desorption and W_o the weight after desorption.



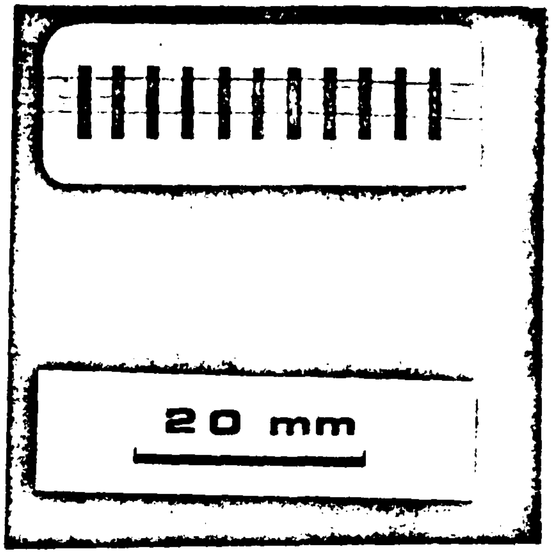


Figure 10: Photograph showing the transparency of the oriented nylon films.

In summary the experimental procedure thus involves:

1. Absorption of anhydrous ammonia at its vapor pressure (~1 MPa) at ambient temperature (43).
2. Retaining of ammonia in the sample by
   a. Cooling to low temperature during transfer to the extruder.
   b. By pressurizing at a pressure > ~5.5 MPa in the Instron which is approximately the vapor pressure of ammonia at 95°C during the extrusion process.
3. Desorption of ammonia at atmospheric pressure at the exit of the extrusion die.

The oriented and transparent films obtained in these experiments shown in Figure 10 were of EDR 11.6 and preliminary property tests indicate by thermal analysis that the crystallinity increased from 23.5% for the originally isotropic film to 53% assuming that the heat of fusion for perfect crystals of nylon 6 is 46.2 cal/gr (44) and the melting point from 219°C to 223°C. The extruded films have a tensile modulus of 13 GPa at 0.1% strain and birefringence 8.25×10^{-2}. These values are higher than those obtained previously from untreated higher nylon analogues deformed in the solid state (45,46). The results thus document the effectiveness of plasticization. A more detailed evaluation of this novel plasticization process which is amenable to other deformation techniques and to thermoplastics with interchain hydrogen bonding is under investigation.

Summary

A variety of new processes have been described that increase the range of the solid state extrusion process for low molecular weight polyethylene and also allow extrusion of a wide range of polymers, polymer morphologies and treated polymers. The factors affecting the solid-state extrusion of polymers may be divided into two main groups, factors associated with the extrusion process and those associated with the polymer itself. Similarly the processes described here may also be divided into these two groups.

The limits to extrusion of polymers by the conventional extrusion process are primarily processing factors. The extrusion pressure cannot exceed a certain value because stick-slip occurs so eventually the viscosity of the material rises so high that the extrusion rate becomes negligible and the extrusion stops. The split billet and push-pull processes combined allowed sufficient loads to be applied to the material to fracture it at the base of the die in a form of elongational failure, i.e. the maximum draw ratio prior to fracture may be obtained. The coextrusion techniques also avoid problems associated with the extrusion process by controlling the dimensions of the components and hence limiting the extrusion pressure, and also removing shear at the edge of the films and at the surface of the core.

The other restriction on the extrusion of polymers is the mechanical properties of the polymer, a restriction that applies to all solid state deformation processes. Two developments reported here are related to the property of the polymers. By using a billet of a compressed powder rather than a melt crystallized billet, the degree of molecular entanglement was greatly reduced and so the extrusion pressure required to deform the material was reduced. Nylon 6 could be deformed much more easily after impregnation with ammonia. The ammonia acts as a reversible plasticizer substantially reducing the force required to deform the material and increasing the elongation before fracture.

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Techniques are reviewed and extended for solid state deformation of semi-crystalline polymers. Emphasis has been placed on solid state extrusion and its variations that include coextrusion, reversible plasticizers and powder deformation. The properties of extrudates are examined in regard to anisotropy with the goals of maximum orientation, tensile properties and the efficiency of deformation.

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